Argonne National Laboratory

PREPARATION OF METALS BY MAGNESIUM-ZINC REDUCTION

Part I Reduction of Uranium Oxides

by

J. B. Knighton and R. K. Steunenberg

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J. B. Knighton and R. K. Steunenberg

Chemical Engineering Division

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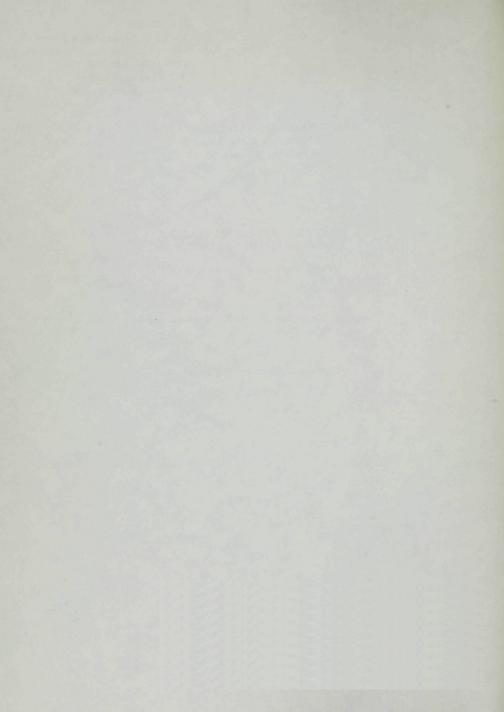


TABLE OF CONTENTS

		Page
ABS	STRACT	4
I.	INTRODUCTION	4
II.	EXPERIMENTAL PROCEDURE	6
III.	RESULTS	7
	A. Flux Composition	7
	B. Temperature	9
	C. Agitation	10
	D. Uranium Oxide Particle Size	10
	E. Quantity of Flux	11
	F. Reduction of Uranium Dioxide and Uranium	
	Tetrafluoride	12
IV.	DISCUSSION	12
v.	CONCLUSIONS	. 15
AC	KNOWLEDGMENT	. 16
RE:	FERENCES	. 17

LET OF FIGURES

Effect of Figuride ion Concentration in the Flux on the Reduction Rate of $U_{\chi}\Omega_{g}$	

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ABSTRACT

The use of liquid magnesium-zinc alloy for the reduction of uranium oxides to the metal has been investigated. The uranium oxide was suspended in a flux composed of alkali and alkaline earth halides and reduced by vigorously mixing the flux-oxide slurry with zinc-5 w/o magnesium alloy at temperatures between 650 and 800°C. The reductions were conducted in an alumina crucible under an air atmosphere. As the uranium metal was produced, it dissolved in the liquid-metal alloy, from which it could later be recovered by vacuum distillation of the zinc and magnesium. The effects of flux composition, temperature, agitation, magnesium oxide loading in the flux, and uranium oxide particle size on the rate and extent of reduction were investigated. Under optimum conditions, over 99% reduction of U3O8 was achieved in periods as short as 10 min on the laboratory scale (4 g of uranium). Uranium losses inherent in the process are well below 1%.

I. INTRODUCTION

Although the reduction of uranium tetrafluoride by magnesium is the primary commercial method for the production of uranium metal, several alternative procedures have been demonstrated and used for special purposes. (1) Magnesium, calcium, carbon, aluminum, silicon, lithium, and sodium have been employed in the reduction of uranium oxides and halides. (1,2) Metallothermic reductions ordinarily involve the "bomb" technique, which utilizes the heat of reaction to coalesce the metallic uranium product and the slag in readily separable masses.

In the case of uranium oxides, a bomb process was developed by Marden, (3) who used calcium as the reducing agent, zinc chloride as a booster, calcium chloride as a flux, and zinc as a collecting agent for the reduced uranium. Bellamy and co-workers (4,5) subsequently developed a bomb procedure for the reduction of uranium dioxide, using calcium and

calcium chloridal or magnesium and magnasium chloride, respectively, as reducing and fluxing agents. Beard and submanuel() usmonal rate fibe reduction of uranium trioxida with deleters to form equivalent uranium particles;

As a possible atternative to the bomb method, liquid-mostal solvental plants been investigated in this laboratory as modified for the reducedor of the function of the functio

Subsequent studies have about this malies tubies tubes distributes offer delight advantages to the reduction of creature codes by mollen metals.

(1) the reduction rates are increased markedly, (1) the integeration oxides by spendies of the link and thereby reported by the flux and thereby reported from the product in the metal phase, and (1) the reduction can, if desired his partners in the cores.

The reduction of U₂O₂ by liquid sinc-magnesium alloy can be rependently on the following ownedle equation:

U.O. (Right # 8Mg (Zn) - 8MgO (Rost) + 3U (Zn-Mg)

The transmo caude, which is dispersed in the flux at a solid, is reduced by the magnesium in the metal phase. The magnesium exide in-product cult-lects in the flux, and the installic eximines product maked we in the single magnes with alloy. Vacuum distillation of the magnesium and sinc from the product solidition forms are madely metal apongs, which can be consolidated by melting.

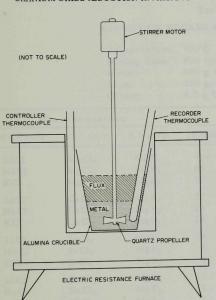
The objective of the present was to investigate the effects of perturent variables on the reduction of UrO, by liquid there was named with an alloy in the presence of these, with supplementary studies of the pedaction of virantum dioxide end unmium terralizantite. Subsequent terra-tigations of a similar technique by the reduction of therims and customium oxides are described to the two indiaway reports. (11,12)

II. EXPERIMENTAL PROCEDURE

The zinc and magnesium used in the reduction studies were of greater than 99.99 and 99.95% purity, respectively. The fluxes were prepared from analytical reagent-grade salts, except for the magnesium chloride, which was obtained from commercial sources as a by-product of the reduction of zirconium tetrachloride by magnesium metal.

The reductions were conducted in a 4-in.-ID, tapered, slip-cast, alumina crucible located in an electrically heated pot furnace (see Figure 1). A temperature controller was actuated by a Chromel-Alumel

Figure 1
URANIUM OXIDE REDUCTION APPARATUS



thermocouple positioned between the inside furnace wall and the outside of the crucible. The temperature inside the crucible was measured with a Chromel-Alumel thermocouple placed inside an alumina thermowell that terminated in the metal phase just below the flux-metal interface. Mixing was provided by a motor-driven quartz propeller on a quartz shaft, with the thermowell serving as a baffle. All the experiments were performed in the laboratory air atmosphere.

In each reduction run, a charge consisting of 400 g of zinc-5 w/o magnesium alloy and 200 g of flux was added to the crucible at room temperature. The charge was then melted, and when the system had reached the operating temperature, mixing was started and the uranium oxide was added to the flux. Sufficient U_3O_8 was used to produce a uranium concentration of 1.0 w/o in the metal phase upon complete reduc-

tion, except where indicated otherwise. Unfiltered metal samples were withdrawn at predetermined time intervals into 6-mm Vycor tubes by a hand-operated, rubber, suction bulb. The samples were then removed from the tubes and analyzed for uranium.

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charge consisting of 400 g of 200 g of 100 g of 100 g of 100 g of 100 g of 200 g of

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III. RESULTS

The influence of the particular variable under study was determined from the percentage of uranium oxide reduced as a function of time.

A. Flux Composition

In the investigations of the effect of flux composition on the reduction of $\rm U_3O_8$, chlorides of the alkali and alkaline earth metals were used as the major flux constituents. A small amount of fluoride (usually magnesium fluoride) was also incorporated into the mixture to achieve a clean, well-defined, flux-metal interface, thereby facilitating rapid coalescence and clean separations of the two phases. The results of a series of survey experiments are summarized in Table I.

Table I SURVEY OF FLUXES FOR U3O8 REDUCTION

Temperature: 750°C Mixing Rate: 800 rpm

Metal: 400 g Zn-5 w/o Mg

Flux: 200 g, composition as shown Oxide: 4.7 g U₃O₈, -325 mesh

Flu	x Composition	on		Percen	t Reduction	n of U ₃ O ₈	
47.5 m/o	47.5 m/o	5.0 m/o	10 min	20 min	30 min	60 min	120 min
LiCl	MgCl ₂	MgF ₂	99+	99+	99+	99+	99+
NaCl	MgCl ₂	MgF ₂	86	99	99	99	99
KCl	MgCl ₂	MgF ₂	71	91	98	97	98
LiCl	CaCl ₂	MgF ₂	27	44	56	86	99+
NaCl	CaCl ₂	MgF ₂	24	31	39	60	84
KCl	Ca Cl ₂	MgF ₂	14	18	21	31	41
LiCl	SrCl ₂	MgF	19	36	47	67	89
NaCl	SrCl ₂	MgF ₂	8	13	21	40	70
KCl	SrCl ₂	MgF ₂	3	4	5	8	10
LiCl	BaCl ₂	MgF ₂	13	22	26	52	85
NaCl	BaCl ₂	MgF ₂	13	20	27	31	45
KCl	BaCl ₂	MgF ₂	4	5	10	18	19
LiCl	NaCl	MgF ₂	6	9	9	13	23
LiCl	KC1	MgF2	4	3	3	6	7
KCl	NaCl	MgF ₂	2	3	3	6	13
	14-C1	MgF ₂	97	99+	99+	99+	99+
CaCl ₂	MgCl ₂	MgF ₂	99	99	99	99	99
SrCl ₂ BaCl ₂	MgCl ₂ MgCl ₂	MgF ₂	92	99	99	99	99
	LiCl	LiF	10	11	12	17	23
LiCl MgCl ₂	MgCl ₂	MgF ₂	98	99+	99+	99+	99+
80 m/o	20 m/o						
CaCl ₂	CaF ₂		6	5	8	11	17

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The influence of the particular variable under study was determined from the percentage of uracium unide rediced as a function of true.

Flux Composition

In the investigations of the effect of flux composition on the raduction of UrOs, chlorades of the sibnit and sibnine earth matain were used as the major flux constituents. A small amount of fluoride (assuity sugmestant fluoride) was also incorporated into the mixture to achieve a clear walldefined, flux-motel interface, thoraby facilitating rapid confessions and clean separations of the two phases. The results of a series of survey experiments are summerized in Table 1.

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SURVEY OF FURNES FOR U.O. REDUCTION

Temperature: 760°C
Mixing Rate: 80% spin-)
Metal: 000°C 20-5 w/o Mg
Flux: 200°C composition as shown
Courde: 0.7 c MyC, 125 mash

These results indicate that the rate and extent of reduction varied markedly with the kind of cations present in the flux, the better reductions occurring with the flux cations of lower atomic weight. When combinations of alkali and alkaline earth chlorides were used, this effect was evident in both cases; that is, the rate and extent of reduction decreased progressively in the order LiCl > NaCl > KCl, and MgCl₂ > CaCl₂ > SrCl₂ > BaCl₂.

Magnesium chloride was a major constituent of all fluxes that resulted in satisfactory reduction rates. All other compositions gave low rates, leading to the conclusion that magnesium chloride is an essential flux ingredient.

Two of the more effective fluxes (LiCl-MgCl₂-MgF₂, and CaCl₂-MgCl₂-MgF₂) were examined further to determine the minimum magnesium cation concentration needed for satisfactory reduction of U₃O₆. The results are listed in Table II. To achieve essentially complete reduction by the zinc-5 w/o magnesium alloy within a practical period of time, the magnesium ion concentration had to correspond to 10 to 20 a/o of the total cations in the flux. Lithium chloride was somewhat superior to calcium chloride as the other major constituent. Although magnesium chloride alone was a satisfactory flux, from the viewpoint of uranium oxide reduction rates, dilution with other chlorides is desirable to lower the melting point and decrease the vapor pressure of the salt.

Table II

EFFECT OF MAGNESIUM ION CONCENTRATION IN THE FLUX
ON THE REDUCTION RATE OF U3O8

Temperature: 750°C
Mixing Rate: 800 rpm
Metal: 400 g Zn-5 w/o Mg
Flux: 200 g, composition as shown
Oxide: 4.7 g U₃O₈, -325 mesh

Flux Composition, m/o			Percent Reduction of U308					
LiCI	MgCl ₂	MgF2	10 min	20 min	30 min	60 min	120 min	
95	0	(5 mole % LiF)	10	11	12	17	23	
95	0	5	6	14	16	25	25	
	-	5	38	59	81	94	99	
90	10	É	61	92	96	99+	99+	
85	10	2	89	99+	99+	99+	99+	
80	15	2	92	95	98	94	96	
75	20	,		99+	99+	99+	95	
70	25	5	95		99+	99+	99+	
47.5	47.5	5	99+	99+			99+	
0	95	5	98	99+	99+	99+	99+	

	Flux Composition m/o	1,	Percent Reduction of U308					
CaCl ₂	MqCl2	MgF2	10 min	20 min	30 min	60 min	120 min	
95ª	0	5	27	41	45	54	53	
	0	5	50	63	71	79	85	
90a	15	-	77	90	96	97	99+	
80	15	. 2	81	93	95	99+	99+	
70	25	2			98	99	97	
65	30	5	90	96				
60	35	5	98	99+	99+	99+	95	
	45	5	96	99	99	95	93	
50		-	98	97	98	96	93	
40	55	,					99+	
0	95	5	98	99+	99+	99+	99+	

^aTemperature, 800°C.

These results indicate that the rate and extent of reduction varied markedly with the blad of dations present in the flux, the being reductions occurring with the flux battons of lower charies weight. When combinations of albait and similar extent chlorides were used, this effect was wriding in both daswiff that its retention extent of reduction decreased pragressically in the order LECT > MaCl. and MgCl. > CaCl. > SaCl. > SaCl.

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A brief study was made to determine the effect of changing the anionic constituents of the flux. Whereas fluoride ion had originally been incorporated into the flux as a means of obtaining good flux-metal separation at the interface, it also appeared to have a beneficial effect on the rate of uranium oxide reduction, as shown in Table III. With fluxes containing 5 m/o magnesium fluoride, over 99% reduction occurred within 20 min; a 30-min period was required in the absence of fluoride.

Table III $\begin{tabular}{ll} EFFECT OF FLUORIDE ION CONCENTRATION IN THE FLUX \\ ON THE REDUCTION RATE OF <math>U_3O_8 \end{tabular}$

Temperature: 750°C Mixing Rate: 800 rpm

Metal: 400 g Zn-5 w/o MgFlux: 200 g, composition as shownOxide: 4.7 g U_3O_8 , -325 mesh

Flux	Composit m/o	tion,	C.F.	Percent	t Reduction	n of U ₃ O ₈	
Ca Cl ₂	MgCl ₂	Mg F ₂	10 min	20 min	30 min	60 min	120 min
50.0	50.0	0	90	96	99+	99+	96
47.5	47.5	5.0	97	99+	99+	99+	99+

B. Temperature

The effect of temperature on the reduction rate was investigated, using the following fluxes: $47.5 \text{ m/o} \text{ CaCl}_2$ - $47.5 \text{ m/o} \text{ MgCl}_2$ - $5.0 \text{ m/o} \text{ MgF}_2$, and 47.5 m/o LiCl- $47.5 \text{ m/o} \text{ MgCl}_2$ - $5.0 \text{ m/o} \text{ MgF}_2$. The results in Table IV show that the reduction rate increased with rising temperature. The temperature dependence of the rate, however, was relatively small. Complete reduction of U_3O_8 was achieved at temperatures as low as 650°C , but higher temperatures are preferred.

Table IV $\begin{tabular}{ll} EFFECT OF TEMPERATURE ON THE REDUCTION RATE \\ OF U_3O_8 \end{tabular}$

Mixing Rate: 800 rpm

Metal: 400 g Zn-5 w/o Mg
Flux: 200 g, composition as shown

Flux: 200 g, composition as s Oxide: 4.7 g U₃O₈, -325 mesh

School Control		arrivant ordi	Percent Reduction of U ₃ O ₈						
Temper (°C)	ature	10 min	20 min	30 min	60 min				
lar es	Flux:	47.5 m/o LiCl - 4	7.5 m/o Mg	Cl ₂ - 5.0 m/o M	gF ₂				
600	Em d	80	95	95	96				
650		79	90	94	99+				
700		97	99+	99+	99+				
750		99+	99+	99+	99+				
	Flux:	47.5 m/o CaCl ₂ -	47.5 m/o Mg	gCl - 5.0 m/o M	gF ₂				
650	TO THE T	77	94	99	99				
700		94	97	99	99				
750		97	99+	99+	99+				

A brief study was made to determine the cilest of changing the suigned constituents of the flux. Whereas fluoride on had originally been incorporated into the flux as a means of obtaining good flux-mainly been ration at the interface, it also appeared to have a beneficial effect on the ratio of uranium oxide reduction, as shown in Table III. With fluxes constituing 5 m/s magnesium fluoride, over 99% reduction occurred within thinks 5 m/s magnesium fluoride, over 99% reduction occurred within the mine absence of fluoride.

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Temperature

The effect of temperature on the reduction rate was investigated, using the following fluxes: 47.5 m/o CaCig-47.5 m/o McCig-5.0 m/o MgTy, and 47.5 m/o LiCl-47.5 m/o MgCig-4.0 m value in the results in Table IV show that the reduction rate increased with rising temperature dependence of the rate, however, was relatively small. Complete reduction of UyOh was achieved at temperatures as lower as 550°C, but higher temperatures are preferred.

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C. Agitation

It was recognized that data on the effect of agitation that could be obtained from laboratory-scale experiments would be unlikely to be applicable to process-scale operation. However, reduction rates shown in Table V, which were obtained at mixing rates of 200, 400, 600, and 800 rpm, indicate that a significant effect exists. Only minor changes in the reduction rate of U3O8 were evident when the mixing rate was lowered from 800 to 400 rpm, but a sharp decrease in the rate was found when the stirring speed was lowered to 200 rpm. For the particular equipment used, a minimum mixing rate between 200 and 400 rpm was necessary to achieve satisfactory reduction rates.

Table V EFFECT OF AGITATION ON THE REDUCTION RATE OF U3O8

Temperature: 750°C

400 g Zn-5 w/o Mg Metal:

200 g 47.5 m/o CaCl₂ - 47.5 m/o Flux:

MgCl₂ - 5.0 m/o MgF₂

4.7 g U₃O₈, -325 mesh Oxide:

3.6:	Percent Reduction of U ₃ O ₈						
Mixing Rate (rpm)	10 min	20 min	30 min	60 min	120 min		
200	4	8	13	34	51		
400	79	99+	94	99+	93		
600	87	99+	99+	99+	99+		
800	77	92	94	98	98 ·		

D. Uranium Oxide Particle Size

Because of the heterogeneous nature of the reaction, the particle size of the U3O8 was expected to influence the reduction rate. Experimental data from a brief study of this effect are given in Table VI. As anticipated, the rate of reduction increased with decreasing particle size of the oxide. Although complete reduction of the coarser oxide was not achieved under these particular conditions, other work(8) has shown that relatively large pieces of uranium oxide (about 1 cm in diameter) can be reduced completely to metallic uranium by this method if more favorable conditions are employed.

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EFFECT OF AGITATION ON THE REDUCTION KATE

1 Branium Oxide Particle Size

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Table VI EFFECT OF PARTICLE SIZE ON THE REDUCTION RATE

OF U3O8

Temperature: 750°C Mixing Rate: 800 rpm

Metal: 400 g Zn-5 w/o Mg

Flux 200 g 47.5 m/o CaCl₂ - 47.5 m/o

MgCl₂ - 5.0 m/o MgF₂

Oxide: 4.7 g U₃O₈

	Percent Reduction of U ₃ O ₈				
U ₃ O ₈ Particle Size	10 min	20 min	30 min	60 min	
-12, +25 mesh	55	76	79	80	
-25, +45 mesh	75	81	79	84	
-80, +170 mesh	87	97	94	99	
-325 mesh	97	99+	99+	99+	

E. Quantity of Flux

The effect of variations in the quantity of flux used on the reduction rate of $\rm U_3O_8$ was investigated, using a $\rm CaCl_2\text{-}MgCl_2\text{-}MgF_2$ flux. In Figure 2, the percentage reduction after various periods of time is shown as a function of the magnesium oxide loading in the flux. In each run, the quantity of $\rm U_3O_8$ charged to the system was sufficient to produce a uranium concentration of 3.92 w/o in the metal phase upon complete reduction. The magnesium oxide loading was calculated from the decrease in magnesium concentration in the metal phase. Additional small amounts of magnesium and calcium oxides or oxychlorides were probably formed by air oxidation of the flux.

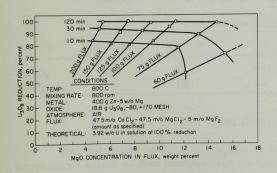


Figure 2 EFFECT OF MAGNESIUM OXIDE LOADING IN FLUX ON U $_3$ O $_8$ REDUCTION



The reduction rate of uranium oxide decreased when the magnesium oxide loading in the flux exceeded about 11 w/o. However, subsequent reductions on a pilot-plant scale with an argon atmosphere were successful with magnesium oxide loadings as high as 15 w/o.(13) At higher loadings, the magnesium oxide caused the flux to become so viscous that it did not provide adequate protection of the liquid metal against oxidation by the air atmosphere. Probably the increased viscosity of the flux also decreased the reduction rates by decreasing the mobility of the unreduced uranium oxide particles.

F. Reduction of Uranium Dioxide and Uranium Tetrafluoride

A few reductions were performed in which uranium dioxide and uranium tetrafluoride were used as the starting materials. Although complete reduction of uranium dioxide occurred with a LiCl-MgCl₂-MgF₂ flux, the rate of reduction was slower than that of U₃O₈ under the same conditions (see Table VII). Uranium tetrafluoride, however, was reduced very rapidly. The uranium tetrafluoride was added to the metal-salt charge at room temperature, and when the system had been heated to 800°C, the liquid-metal phase was sampled before the stirrer was started. Additional samples were then taken after the system had been agitated for periods of 10, 20, 30, 60, and 120 min. Analyses of these samples showed that the uranium tetrafluoride had been completely reduced by the time the first sample was taken before starting the stirrer.

Table VII

REDUCTION RATES OF U3O8 AND URANIUM DIOXIDE

Temperature: 750°C Mixing Rate: 800 rpm

Metal: 400 g Zn-5 w/o Mg

Flux: 200 g 47.5 m/o LiCl-47-5 m/o

MgCl₂-5.0 m/o MgF₂

Oxides: 4.7 g U₃O₈; 4.5 g UO₂

	Percent Reduction of Oxide					
Oxide	10 mim	20 min	30 min	60 min	120 min	
U ₃ O ₈	99+	99+	99+	99+	99+	
UO ₂	78	88	86	96	99+	

IV. DISCUSSION

The solubility of U_3O_8 in the salt is believed to have a bearing on the pronounced effect of flux composition on the reduction rate, although there is little doubt that other factors are also important. The rapid reduction

The reduction rate of uranjum miles decreased when the magnesians oxide loading in the flux exceeded should like on the flux exceeded should like on the flux oxide loadings with an algor atmosphere were successful with magnesium oxide loadings as high as 15 w/o. (11) At higher loadings the flux to become so viscous that it did not provide adequate protection of the flux in mantal against exclusion by the sir atmosphere. Probably the increased viscouity of the flux also decreased atmosphere. Probably the increased viscouity of the flux also decreased the reduction rates by decreasing the mobility of the unreduced uranium oxide particles.

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REDUCTION RATES OF U.O. AND URANIUM DIOXIDE

Temperature: 750°C

Mixing Rate: 800 rpm

Metal: 400 g Zn-5 w/o Mg

Flux: 200 g 47.5 m/o LiCl-47-5 m/o

MgCl₂-5.0 m/o MgF₂

Oxides: 4.7 g U-Oc 4.5 g UO₂

IV. DISCUSSION

The solubility of U₂O₂ in the said is believed to have a bearing on the pronounced wifeet of flux composition on the reduction rate, although there we hattle doubt that other factors are also important. The rapid reduction

rates obtained with fluxes containing a large proportion of magnesium chloride are attributed to a series of reactions of the oxide with the flux, which produce soluble uranium species that are available for reaction with magnesium at the salt-metal interface. The following series of reactions has been postulated on the basis of a separate chemical study of uranium oxidemolten chloride systems: (14,15)

$$U_3O_8 \text{ (solid)} + MgCl_2 \text{ (solution)} \rightarrow MgUO_4 \text{ (solid)} + 2UO_2Cl \text{ (solution)};$$
 (2)

$$MgUO_4$$
 (solid) + $MgCl_2$ (solution) $\rightarrow UO_2Cl_2$ (solution) + $2MgO$ (solid); (3)

$$UO_2Cl_2$$
 (solution) $\neq UO_2Cl$ (solution) + 1/2 Cl_2 (gas). (4)

Magnesium uranate produced by reaction (2) has been isolated from magnesium chloride as a crystalline, reddish-brown solid which has a low solubility in the salt. Other uranates were isolated from fluxes that did not contain magnesium chloride.(16) For example, calcium uranate was isolated from a LiCl-CaCl₂ flux, and potassium uranate from a LiCl-KCl flux to which $\rm U_3O_8$ had been added. These other uranates appeared to be less soluble and less easily reduced than magnesium uranate, which probably accounts for the superiority of magnesium chloride-based fluxes for $\rm U_3O_8$ reduction.

The uranyl(V) chloride produced by reactions (2) and (4) has been characterized as a soluble species with a distinctive absorption spectrum. (14,15) Upon continued exposure to magnesium chloride, magnesium uranate has been shown to react further to form additional uranyl(V) chloride in solution, and solid magnesium oxide, as indicated by reaction (3). The thermal decomposition of uranyl(VI) chloride, reaction (4), has been shown by a combination of spectrophotometric and pressure measurements to have an equilibrium constant of about 10⁻⁶ atm at 650°C.

In the presence of the magnesium-zinc alloy, uranyl(V) chloride appears to be readily reduced to metallic uranium:

$$2UO_2Cl (flux) + 5Mg (Zn) \rightarrow 2U (Mg-Zn) + 4MgO (flux) + MgCl_2 (flux).$$
 (5)

It is reasonable to expect that any chlorine formed by reaction (4) would combine readily with the magnesium:

$$Mg(Zn) + Cl_2(gas) \rightarrow MgCl_2(flux).$$
 (6)

By combining reactions (2) through (6), one arrives at the overall reaction indicated by equation (1).

Uranium dioxide exhibits a lower solubility than U_3O_8 in fluxes of this general type. For example, a solubility value of about $10^{-2} \, \text{w/o}$ was

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UpO, (solid) + MgClg (solution) - MgUO; (solid) s 2UO; (solid) s 2UO;

MgDO, (solid) + MgCla (solution) = UO_Cla (solution) 4 MgCla (solid);

DOCCI, (selution) # UO.Cl (solution) + 1/2 Cl. (gas).

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observed at 500° C in a flux composed of 30 m/o NaCl, 20 m/o KCl, and 50 m/o MgCl₂. (17) Furthermore, solid uranium dioxide has been indentified as such after extended exposure to the flux, indicating that it is not converted to a more soluble species by reaction with magnesium chloride. Thus, the slower reduction rate of uranium dioxide is ascribed primarily to the fact that only a relatively low concentration in solution is available at the salt-metal interface.

In contrast, uranium tetrafluoride, which was completely soluble in the flux at the concentrations used, was reduced very rapidly. Uranium chlorides, which also have high solubilities, would be expected to behave similarly.

No attempt was made to investigate the reduction rates of uranium trioxide in this study, as it is known to decompose at 650°C to form U_3O_8 : (18)

$$3UO_3 \text{ (solid)} \rightarrow U_3O_8 \text{ (solid)} + 1/2 O_2 \text{ (gas)}.$$
 (7)

In the choice of a flux for process purposes, practical considerations, in addition to its effect on uranium oxide reduction rates, must be taken into account. For example, magnesium chloride alone provides satisfactory reduction rates, but additions of alkali and alkali metal chlorides are useful in lowering the melting point and decreasing the vapor pressure. Small additions of fluoride produce a clean flux-metal interface, permitting a much cleaner separation of the two phases.

When the liquid-metal solvent was selected, the zinc-5 w/o magnesium system was chosen primarily because several investigators(7,8,10) had observed optimum reduction of uranium oxides by this alloy. The solid phase in equilibrium with a uranium-saturated solution of this composition is a uranium-zinc intermetallic compound of the approximate composition UZn_{11.5}. The free energy of formation of this compound, -15 kcal/g-atom of uranium at 750°C,(19) provides an additional driving force for reaction (1). Magnesium concentrations below about 5 w/o are undesirable because of the unfavorable mass action effect on reaction (1), and increasing the concentration much above this value has the adverse effect of increasing the activity coefficient of the uranium, which is also unfavorable to reaction (1).

Since the effect of changing temperature on the reduction rate is small, other factors are of greater importance in choosing an operating temperature. For example, a lower temperature limit is set by the melting point of the flux. In addition, if the process involves a subsequent transfer of the liquid-metal product solution, reasonably high uranium solubilities are desirable. The solubility of uranium in zinc-5 w/o magnesium is 0.42 w/o at 650°C and 5.2 w/o at 800°C .(20) On the other hand,

charged at Sport in a first component of the major NaCl. 20 m/o NCl, and Sh major MgCl., (17) Expendences, solid uranium dioxide has been indentified an authority while it is not feet an authority while it is not feet to use flux, which while it is not converted to use considerable appropriate to use flux with majorary considerable appropriate to a satisfied maintain the feet that time a satisfied propriate to a columbia the appropriate an columbia of available at the salt-inmiss before

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the maximum temperature is limited by the vapor pressure of zinc. To prevent excessive zinc vaporization, it was found desirable to limit the temperature to about 100°C below the boiling point of zinc (910°C).

The observations that the mixing rate, the particle size of the uranium oxide, and the viscosity of the flux all effect the reduction rate, and that the more soluble uranium tetrafluoride undergoes rapid reduction, suggest that the reaction of the oxide with the flux is very likely the rate-controlling step in the process.

In this study, no attempt was made to recover consolidated uranium metal from the zinc-magnesium alloy. However, vacuum distillation of this solvent to recover uranium has been demonstrated on a kilogram scale, (21) and consolidation of metallic sponges by melting is a standard operation.

Since a consolidated uranium product was not recovered in these experiments, specific data are not available on the impurity content of the product. In reductions of thorium and plutonium oxides, however, the metallic product was of higher purity than the oxides that were used as the starting material.(11,12) Electropositive elements, such as alkali and alkaline earth metals are retained in the flux during the reduction. Magnesium and zinc can be removed by standard retorting methods to levels of less than 300 and 100 ppm, respectively.(13)

V. CONCLUSIONS

These laboratory-scale studies show that $\rm U_3O_8$ can readily be reduced to metallic uranium by magnesium-zinc alloy in simple equipment in an air atmosphere. A molten halide flux is used to increase the reaction rate, to collect the solid magnesium oxide formed as a by-product, and to protect the magnesium-zinc alloy from oxidation by the air. Magnesium chloride appears to be an essential ingredient of the flux, and the presence of a small amount of fluoride in a predominantly chloride flux is beneficial.

Zinc-5 w/o magnesium alloy is an effective reductant, since it provides rapid, complete reduction when used with an appropriate flux, and it can be removed from the metallic uranium product by distillation.

Although complete reduction of U_3O_8 was achieved at temperatures as low as 650°C, operation at 750 to 800°C offers the benefits of a wider choice of flux composition, higher uranium solubility in the metal phase, and somewhat faster reduction rates.

Good mixing is required for satisfactory reduction rates. The reduction rate decreases with increasing particle size of the oxide, but very

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large particles can be completely reduced. The magnesium oxide byproduct has an adverse effect on the reduction rate when the amount exceeds about 10 to 15% of the weight of flux used.

The method appears to be generally applicable to the oxides and the lower chlorides and fluorides of uranium. These studies were conducted on a small scale (\sim 5 g uranium), but subsequent work has shown that $\rm U_3O_8$ reduction on a 2-kg scale by this method is feasible.(13) The uranium losses inherent in the process are less than 1%.

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